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January 18, 2002

BOX PCT
Commissioner for Patents
Washington, D.C. 20231

PCT/EP00/08057
-filed August 17, 2000

Re: Application of Didier HAAS, Claude FUCHS, Serge FOURCAUDOT, Francois CHAROLLAIS and Joseph SOMERS
METHOD FOR PRODUCING NUCLEAR FUEL PELLETS OF THE MOX TYPE
Assignee: EUROPEAN COMMUNITY (EC)
Our Ref: Q67836

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

☑ an executed Declaration and Power of Attorney.

☑ a copy of the International Publication

☑ Notification Concerning Submission or Transmittal of Priority Document.

☑ an executed Assignment and PTO 1595 form.

☑ International Search Report, Information Disclosure Statement and a Form PTO-1449.

It is assumed that copies of the International Application, the International Search Report, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

Applicant claims benefit of small entity status in accordance with 37 CFR § 1.27.

The Government filing fee is calculated as follows **(Small Entity fees apply)**:

Total claims	12	-	20	=	_____	x	$9.00	= $.00
Independent claims	1	-	3	=	_____	x	$42.00	= $.00
Base Fee								$445.00
Multiple Dependent Claim Fee								$140.00
TOTAL FILING FEE								$585.00
Recordation of Assignment								$ 40.00
TOTAL FEE								$625.00

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Checks for the statutory filing fee of $585.00 and Assignment recordation fee of $40.00 are attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from:

Country	Application No	Filing Date
European	99116886.5	September 6, 1999

Respectfully submitted,

Sheldon I. Landsman

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SIL/amt

10/031407
JC13 Rec'd PCT/PTO 18 JAN 2002
PCT/EP00/08057

METHOD FOR PRODUCING NUCLEAR FUEL PELLETS OF THE MOX TYPE

This invention refers to a method for producing nuclear fuel pellets of the MOX (= mixed oxide) type, comprising the steps of

- preparing an U-Pu oxide blend powder having a Pu content in excess of the finally desired value,
- preparing an uranium oxide powder,
- mixing adequate quantities of both powders in order to achieve the desired plutonium content,
- compacting and sintering the mixture for obtaining said pellets.

Such a method is known under the term MIMAS ("MIcronized MASter Blend" - see for example D. Haas, M. Lippens "MOX FUEL FABRICATION AND IN-REACTOR PERFORMANCE", Proc. of the Internat. Conference on Future Nuclear Systems, GLOBAL 97, p.489 à 494). This separate preparation of a powder free of plutonium reduces the volume of plutonium containing powder that has to be milled, and allows the production of fuel pellets of various plutonium contents with a unique plutonium treatment chain by changing only the rate of admixed uranium powder.

The commercial powders currently used, however, result in a final product which is heterogeneous, i.e. contains large particles rich in plutonium oxide dispersed within an uranium oxide matrix whose grain size is below 10 µm. This heterogeneity leads to two major drawbacks:

During irradiation localised higher fissile material concentrations lead to high local burnups, to fission damages and to gas release. To limit this gas release large UO_2 grains are recommended, provided that they are produced without additives that might lead to detrimental fuel behaviour during irradiation and might also lead to difficulties during reprocessing.

During reprocessing the dissolution of the burned-up fuel in nitric acid is hindered by regions rich in pluto-

nium, which is notoriously insoluble.

The present invention aims to overcome these drawbacks and to propose a method as indicated above which leads to fuel pellets of the MOX type in which the distribution of plutonium throughout the pellet is substantially more homogeneous.

This aim is achieved by the method as defined in claim 1. As far as preferred embodiments of this method are concerned, reference is made to the secondary claims.

The invention will now be described in detail by means of preferred embodiments.

In agreement with the known MIMAS method as cited above, the method according to the invention implies the separate preparation of a Pu-U oxide powder on the one hand and an uranium oxide powder free of plutonium on the other hand.

According to a first embodiment the Pu-U oxide powder is prepared conventionally by mechanically milling PuO_2 and UO_2 materials, whereas the UO_2 powder is prepared as follows:

To an aqueous solution of uranyl nitrate small amounts, i.e. between 0.5 and 2 wt%, of organic thickeners are added, such as methocel, dextran, polyvinyl alcohol, such that the viscosity of the solution is adjusted to values between 20 and 100 centipoise. There-after, this solution is dispersed into droplets, which are introduced into an ammonia bath. In this bath, due to the network formed by the long chain organic polymers, precipitation occurs within the original droplets, so that nearly spherical beads are formed. The size of these beads depends on the size of the droplets produced during dispersion. In a preferred embodiment these beads present diameters of between 20 and 50 µm. These beads are then washed to remove nitrate salts (ammonium nitrate salts in the above example) and organic polymers, and are subjected to an azeotropic distillation using an immiscible organic solvent such as C_2Cl_4 to

remove water.

Once dried the beads are in a hydroxide form, from which they are converted to oxide by a thermal treatment of between 2 and 6 hours duration and at about 400°C in air. Thereby residual organic polymers are pyrolysed. The beads are then again submitted to a thermal treatment of between 4 and 8 hours duration, this time at about 800°C and in a reducing atmosphere of $Ar/5\%H_2$, to convert U_3O_8 to UO_2.

The beads can be produced by conventional uranium processing facilities (no α contamination). They are free flowing, dust free and do not require any further mechanical treatment such as milling prior to mixing with the powder containing plutonium. The homogeneity of the finally produced fuel can further be enhanced by sieving the beads and retaining only beads with diameters in the range of 20 to 50µm. Alternatively this result can also be achieved by using a droplet dispersion device which produces droplets of well defined size such that the bead diameters remain within said range and no sieving becomes necessary.

Once mixed the MOX powder is compacted into pellets by using a press which applies a pressure of between 200 and 600 MPa. These pellets are then sintered at high temperature, preferably at 1700°C, in a humidified Ar/H_2 atmosphere, the hydrogen content of which lies between 1 and 6% and the water vapour introduction should result in a ratio of the partial H_2 pressure to the water vapour partial pressure of between 20 and 60. The water allows to control the oxygen potential of the gas atmosphere which results in an enhanced diffusion and in a more homogeneous fuel thus enabling a longer burn-up in the reactor.

According to a variant of the method the powder containing an excess content of plutonium can be prepared in the same way as above described for the uranium oxide powder, but by starting with uranyl-plutonium nitrate instead of uranyl nitrate.

The inventive method can be realised in conventional MOX fabrication facilities and conserves all the advantages of the MIMAS process but does not suffer from the drawbacks of this process as mentioned above.

CLAIMS

1. A method for producing nuclear fuel pellets of the MOX (mixed plutonium and uranium oxide) type, comprising the steps of

- preparing an U-Pu oxide blend powder having a Pu content in excess of the finally desired value,
- preparing an uranium oxide powder,
- mixing adequate quantities of both powders in order to achieve the desired plutonium content,
- compacting and sintering the mixture for obtaining said pellets,

characterized in that the step of preparing the uranium oxide powder involves the following sequence of substeps:

a) preparation of an aqueous solution of uranyl nitrate to which between 0.5 and 2 wt% of organic thickeners are added such that the viscosity of the solution is adjusted to values between 20 and 100 centipoise,

b) dispersion of the solution into droplets,

c) introducing said droplets into a hydroxide bath,

d) washing the resulting beads,

e) drying the beads by azeotropic distillation using an immiscible organic solvent,

f) thermal treatment of the beads in an oxidising atmosphere,

g) thermal treatment in a reducing atmosphere.

2. A method according to claim 1, characterized in that the step of preparing an U-Pu oxide blend powder consists in milling and mixing adequate quantities of uranium oxide and plutonium oxide.

3. A method according to claim 1, characterized in

that the step of preparing the U-Pu oxide blend powder involves the following sequence of substeps:

a) preparation of an aqueous solution of uranyl-plutonium nitrate to which small amounts of organic thickeners are added in order to adjust the viscosity of the solution to values between 20 and 100 centipoise,

b) dispersion of the solution into droplets,

c) introducing said droplets into a hydroxide bath,

d) washing the resulting beads,

e) subjecting the beads to an azeotropic distillation using an immiscible organic solvent,

f) thermal treatment of the beads in an oxidising atmosphere,

g) thermal treatment in a reducing atmosphere.

4. A method according to anyone of the preceding claims, characterized in that in substep a) the organic thickeners are selected among methocel, dextran and polyvinyl alcohol.

5. A method according to anyone of the preceding claims, characterized in that in substep c) the hydroxide bath consists of ammonia.

6. A method according to anyone of the preceding claims, characterized in that in substep f) the thermal treatment in an oxidising atmosphere is performed at about 400°C and in air.

7. A method according to anyone of the preceding claims, characterized in that in substep g) the thermal treatment in a reducing atmosphere is performed at about 800°C, the reducing atmosphere containing an inert gas with a hydrogen content between 1 and 6%.

8. A method according to anyone of the preceding claims, characterized in that compacting of the powder mixture into pellets is obtained by applying a pressure of between 200 and 600 MPa.

9. A method according to anyone of the preceding claims, characterized in that the sintering of the pellets takes place at a temperature above 1200°C, preferably between 1600 and 1700°C, and in a humidified Ar/H_2 atmosphere, the hydrogen content lying between 1% and 6% and the ratio between the partial pressures of hydrogen and water vapour being selected between 20 and 60.

10. A method according to anyone of the preceding claims, characterized in that before mixing adequate quantities of both powders, the UO_2-powder is sieved in order to retain only beads with diameters between 20 and 50µm size.

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DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name: that I verily believe I am the original, first and sole inventor (if only one name is listed below) or a joint inventor (if plural names are listed below) of the subject matter claimed and for which a patent is sought in the application entitled:

which application is:
___ the attached application
(for original application)

PCT application Serial No. PCT/EP00/08057
filed Aug.17,2000, and amended on
___
(for declaration not accompanying application)

that I have reviewed and understand the contents of the specification of the above-identified application, including the claims, as amended by any amendment referred to above; that I acknowledge my duty to disclose information of which I am aware which is material to the patentability of this application under 37 C.F.R. 1.56, that I hereby claim foreign priority benefits under Title 35, United States Code §119, §172 or §365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified on said list any foreign application for patent or inventor's certificate on this invention having a filing date before that of the application on which priority is claimed:

Application Number	Country	Filing Date	Priority Claimed (yes or no)
99116886.5	Europe	Sept. 6, 1999	yes

I hereby claim the benefit of Title 35, United States Code §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in a listed prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge my duty to disclose any information material to the patentability of this application under 37 C.F.R. 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status (patented, pending, abandoned)

I hereby appoint John H. Mion, Reg. No. 18,879; Donald E. Zinn, Reg. No. 19,046; Thomas J. Macpeak, Reg. No. 19,292; Robert J. Seas, Jr., Reg. No. 21,092; Darryl Mexic, Reg. No. 23,063; Robert V. Sloan, Reg. No. 22,775; Peter D. Olexy, Reg. No. 24,513; J. Frank Osha, Reg. No. 24,625; Waddell A. Biggart, Reg. No. 24,861; Robert G. McMorrow, Reg. No. 19,093; Louis Gubinsky, Reg. No. 24,835; Neil B. Siegel, Reg. No. 25,200; David J. Cushing, Reg. No. 28,703; John R. Inge, Reg. No. 26,916; Joseph J. Ruch, Jr., Reg. No. 26,577; Sheldon I. Landsman, Reg. No. 25,430; Richard C. Turner, Reg. No. 29,710; Howard L. Bernstein, Reg. No. 25,665; Alan J. Kasper, Reg. No. 25,426; Kenneth J. Burchfiel, Reg. No. 31,333; Gordon Kit, Reg. No. 30,764; Susan J. Mack, Reg. No. 30,951; Frank L. Bernstein, Reg. No. 31,484; Mark Boland, Reg. No. 32,197; William H. Mandir, Reg. No. 32,156; Scott M. Daniels, Reg. No. 32,562; Brian W. Hannon, Reg. No. 32,778 and Abraham J. Rosner, Reg. No. 33,276, my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and request that all correspondence about the application be addressed to SUGHRUE, MION, ZINN, MACPEAK & SEAS, 2100 Pennsylvania Avenue, N.W., Washington, D.C. 20037-3202.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date 05/05/00

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